Chapter 1
Applying Förster-Type Nonradiative Energy Transfer Formalism to Nanostructures with Various Directionalities: Dipole Electric Potential of Exciton and Dielectric Environment

In this chapter, we present analytical equations for the exciton electric potential inside and outside a nanostructure; including analytical expressions, for the long distance approximation, which are derived for the outside electric potential. Finally, the effective dielectric constant expressions, for this limit, are obtained. This chapter is reprinted (adapted) with permission from Ref. [1]. Copyright 2013 American Chemical Society.

1.1 Spherical Geometry: Nanoparticle Case

The electric potential for an exciton in the α-direction $(\alpha = x, y, z)$, illustrated in Fig. 1.1a, is given by

$$\Phi_\alpha^{in} = \left(\frac{ed_{exc}}{\varepsilon_{NP}}\right)\frac{\hat{\boldsymbol{\alpha}}\cdot\mathbf{r}}{r^3}\left(1 + \frac{2(\varepsilon_{NP} - \varepsilon_0)}{\varepsilon_{NP} + 2\varepsilon_0}\frac{r^3}{R_{NP}^3}\right) \tag{1.1}$$

$$\Phi_\alpha^{out} = \left(\frac{ed_{exc}}{\varepsilon_{NP}}\right)\left(\frac{3\varepsilon_{NP}}{\varepsilon_{NP} + 2\varepsilon_0}\right)\frac{\mathbf{r}\cdot\hat{\boldsymbol{\alpha}}}{r^3} \tag{1.2}$$

where ε_{NP} and ε_0 are the nanoparticle (NP) and medium dielectric constants, respectively. The electric potential is the same in any direction because of the spherical symmetry of the NP. In the long distance approximation the outside electric potential can be written as

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$$\Phi_{\alpha}^{out} = \left(\frac{ed_{exc}}{\varepsilon_{eff}}\right)\frac{\mathbf{r}\cdot\hat{\boldsymbol{\alpha}}}{r^3} \tag{1.3}$$

where ε_{eff} is the effective dielectric constant given by

$$\varepsilon_{eff} = \frac{\varepsilon_{NP} + 2\varepsilon_0}{3} \tag{1.4}$$

1.2 Cylindrical Geometry: Nanowire Case

In this case, the electric potential for an α-exciton $(\alpha = x, y, z)$, illustrated in Fig. 1.1a, is

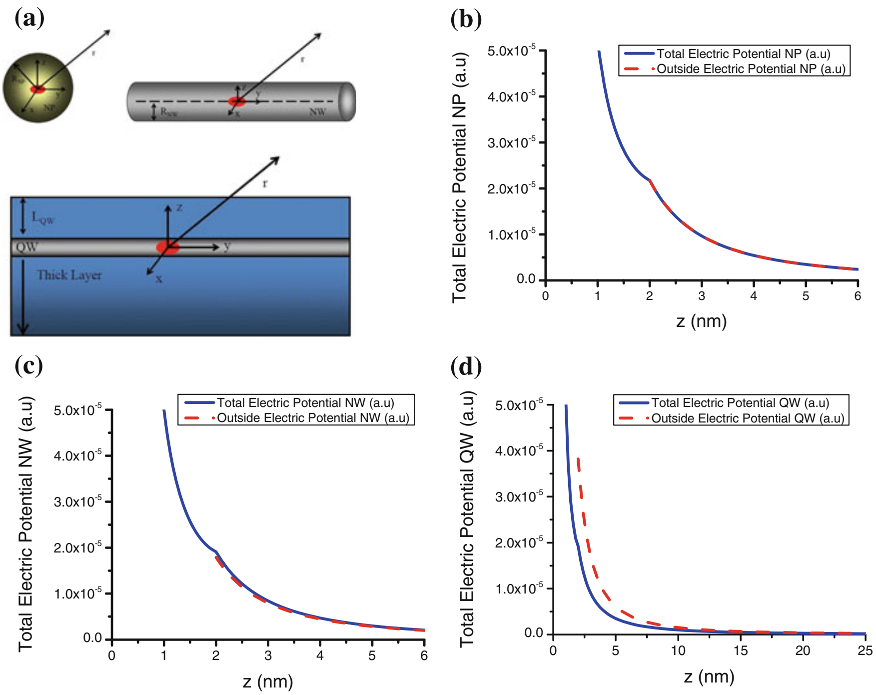

Fig. 1.1 **a** Schematic of an exciton in an NP, an NW, and a QW. *Red circle* represents an exciton in the α-direction. $R_{NP(NW)}$ is the NP (NW) radius. L_{QW} is the QW capping layer thickness. **b**, **c**, and **d** Electric potential along the "z" axis for a z-exciton. Total and long distance approximation electric potential for the z-exciton inside: **b** an NP; **c** an NW; and **d** a QW [Reprinted (adapted) with permission from Ref. [1] (Copyright 2013 American Chemical Society)]

$$\Phi_{\alpha}^{in} = \Phi_{\alpha} + \sum_{m} \int \left(e^{\mathrm{i}m\varphi} \mathrm{e}^{-\mathrm{i}ky} A_{m}^{\alpha}(k) I_{m}(|k \,|\, \rho) \right) dk \tag{1.5}$$

$$\Phi_{\alpha}^{out} = \Phi_{\alpha} + \sum_{m} \int \left(\mathrm{e}^{\mathrm{i}m\varphi} \mathrm{e}^{-\mathrm{i}ky} B_{m}^{\alpha}(k) K_{m}(|k \,|\, \rho) \right) dk \tag{1.6}$$

where $I_m(|k \,|\, \rho)$ and $K_m(|k \,|\, \rho)$ are the modified Bessel functions of order m, and Φ_α is the α-exciton electric potential. After applying the boundary conditions at the surface of the nanowire (NW), the coefficients A_m^α and B_m^α are

$$A_{m}^{\alpha}(k) = \left(\frac{K_m(|k \,|\, R_{NW})}{I_m(|k \,|\, R_{NW})} \right) B_{m}^{\alpha}(k) \tag{1.7}$$

$$B_{m}^{\alpha}(k) = \frac{\frac{2}{|k|}(\varepsilon_0 - \varepsilon_{NW}) g_{m}^{\alpha}(|k|)}{\varepsilon_{NW} \left(\frac{K_m(|k \,|\, R_{NW})}{I_m(|k \,|\, R_{NW})} \right) I_m(|k \,|\, R_{NW}) + \varepsilon_0 K_m(|k \,|\, R_{NW})} \tag{1.8}$$

where $I_m(|k \,|\, R_{NW}),\ K_m(|k \,|\, R_{NW})$, and $g_m^\alpha(|k|)$ are defined as

$$I_m(|k \,|\, R_{NW}) = I_{m-1}(|k \,|\, R_{NW}) + I_{m+1}(|k \,|\, R_{NW}) \tag{1.9}$$

$$K_m(|k \,|\, R_{NW}) = K_{m-1}(|k \,|\, R_{NW}) + K_{m+1}(|k \,|\, R_{NW}) \tag{1.10}$$

$$g_{m}^{\alpha}(|k|) = \frac{1}{(2\pi)^2} \int_{0}^{2\pi} \int_{-\infty}^{\infty} d\varphi dy \mathrm{e}^{-\mathrm{i}m\varphi} \mathrm{e}^{\mathrm{i}ky} \left[\frac{\partial \Phi_\alpha}{\partial \rho} \right]_{\rho = R_{NW}} \tag{1.11}$$

For an exciton in the y-direction (along the cylinder axis), the coefficient B_m^y becomes

$$B_{0}^{y}(k) = \left(\frac{ed_{exc}}{\varepsilon_{NW}} \right) (\varepsilon_{NW} - \varepsilon_0) \frac{i}{\pi} |k| \left(\frac{1}{\left(\frac{K_0(|k| R_{NW}) I_1(|k| R_{NW})}{K_1(|k| R_{NW}) I_0(|k| R_{NW})} \right) \varepsilon_{NW} + \varepsilon_0} \right) \tag{1.12}$$

with an electric potential given by

$$\Phi_{y}^{out} = \left(\frac{ed_{exc}}{\varepsilon_{NW}} \right) \frac{y}{(\rho^2 + y^2)^{\frac{3}{2}}} + \int \left(\mathrm{e}^{-\mathrm{i}ky} B_{0}^{y}(k) K_0(|k \,|\, \rho) \right) dk \tag{1.13}$$

In the long distance approximation, the coefficient B_m^y and the outside electric potential are simplified as

$$B_0^y(k) = \left(\frac{ed_{exc}}{\varepsilon_{NW}}\right)(\varepsilon_{NW} - \varepsilon_0)\frac{i}{\pi}|k|\left(\frac{1}{\varepsilon_0}\right) \tag{1.14}$$

$$\Phi_y^{out} = \left(\frac{ed_{exc}}{\varepsilon_{eff}}\right)\frac{y}{(\rho^2 + y^2)^{\frac{3}{2}}} \tag{1.15}$$

where ε_{eff} is the effective dielectric constant defined as

$$\varepsilon_{eff} = \varepsilon_0 \tag{1.16}$$

In the case of an exciton in the z-direction (perpendicular to the cylinder axis), the coefficient B_m^z which remains as B_1^z and B_{-1}^z, where B_1^z is given

$$B_1^z(k) = \left(\frac{ed_{exc}}{\varepsilon_{NW}}\right)(\varepsilon_0 - \varepsilon_{NW})\frac{|k|}{2\pi}\left(\frac{4}{3}\right)\frac{\frac{\left(\frac{1}{(|k|R_{NW})^2}G_{1,3}^{2,1}\left(\left(\frac{|k|R_{NW}}{2}\right)^2\middle|\begin{matrix}-\frac{1}{2}\\0,1,\frac{1}{2}\end{matrix}\right)-K_2(|k|R_{NW})\right)}{(K_0(|k|R_{NW})+K_2(|k|R_{NW}))}}{\frac{K_1(|k|R_{NW})}{I_1(|k|R_{NW})}\left(\frac{I_0(|k|R_{NW})+I_2(|k|R_{NW})}{K_0(|k|R_{NW})+K_2(|k|R_{NW})}\right)\varepsilon_{NW}+\varepsilon_0} \tag{1.17}$$

and $G_{1,3}^{2,1}\left(\left(\frac{|k|R_{NW}}{2}\right)^2\middle|\begin{matrix}-\frac{1}{2}\\0,1,\frac{1}{2}\end{matrix}\right)$ is the Meijer G-function and $B_1^z = B_{-1}^z$. The electric potential is simplified as

$$\Phi_z^{out} = \left(\frac{ed_{exc}}{\varepsilon_{NW}}\right)\frac{\rho\cos(\varphi)}{(\rho^2 + y^2)^{\frac{3}{2}}} + 2\cos(\varphi)\int\left(e^{-iky}B_1^z(k)K_1(|k|\rho)\right)dk \tag{1.18}$$

In the long distance approximation, the coefficient B and the electric potential become

$$B_1^z(k) = -\left(\frac{ed_{exc}}{\varepsilon_{NW}}\right)(\varepsilon_0 - \varepsilon_{NW})\frac{1}{2\pi}|k|\left(\frac{1}{\varepsilon_{NW} + \varepsilon_0}\right) \tag{1.19}$$

$$\Phi_z^{out} = \left(\frac{ed_{exc}}{\varepsilon_{eff}}\right)\frac{\rho\cos(\varphi)}{(\rho^2 + y^2)^{\frac{3}{2}}} \tag{1.20}$$

where ε_{eff} is the effective dielectric constant defined as

$$\varepsilon_{eff} = \frac{\varepsilon_{NW} + \varepsilon_0}{2} \tag{1.21}$$

Similarly, for an exciton in the x-direction (perpendicular to the cylinder axis), the non-zero coefficients are B_1^x and B_{-1}^x, where B_1^x is given by

$$B_1^x(k) = \left(\frac{ed_{exc}}{\varepsilon_{NW}}\right)(\varepsilon_0 - \varepsilon_{NW})(-i)\frac{|k|}{2\pi}\left(\frac{4}{3}\right)\frac{\frac{\left(\frac{1}{(|k\,|\,R_{NW})^2}G_{1,3}^{2,1}\left(\left(\frac{|k|R_{NW}}{2}\right)^2\middle|\begin{matrix}-\frac{1}{2}\\0,1,\frac{1}{2}\end{matrix}\right)-K_2(|k|R_{NW})\right)}{(K_0(|k|R_{NW})+K_2(|k|R_{NW}))}}{\frac{K_1(|k|R_{NW})}{I_1(|k|R_{NW})}\left(\frac{I_0(|k|R_{NW})+I_2(|k|R_{NW})}{K_0(|k|R_{NW})+K_2(|k|R_{NW})}\right)\varepsilon_{NW}+\varepsilon_0} \tag{1.22}$$

with $B_{-1}^x = -B_1^x$ and the electric potential

$$\Phi_x^{out} = \left(\frac{ed_{exc}}{\varepsilon_{NW}}\right)\frac{\rho\sin(\varphi)}{(\rho^2+y^2)^{\frac{3}{2}}} + i2\sin(\varphi)\int\left(\mathrm{e}^{-\mathrm{i}ky}B_1^x(k)K_1(|k\,|\,\rho)\right)dk \tag{1.23}$$

the coefficients B and the outside electric potential, in the long distance approximation, are simplified as

$$B_1^x(k) = \left(\frac{ed_{exc}}{\varepsilon_{NW}}\right)(\varepsilon_0 - \varepsilon_{NW})\frac{i}{2\pi}|k|\left(\frac{1}{\varepsilon_{NW}+\varepsilon_0}\right) \tag{1.24}$$

$$\Phi_x^{out} = \left(\frac{ed_{exc}}{\varepsilon_{eff}}\right)\frac{\rho\sin(\varphi)}{(\rho^2+y^2)^{\frac{3}{2}}} \tag{1.25}$$

where ε_{eff} is the effective dielectric constant, which is defined as

$$\varepsilon_{eff} = \frac{\varepsilon_{NW}+\varepsilon_0}{2} \tag{1.26}$$

1.3 Planar Geometry: Quantum Well Case

The electric potential, in cylindrical coordinates, for an α-exciton $(\alpha = x, y, z)$, illustrated in Fig. 1.1a, is

$$\Phi_\alpha^{in} = \Phi_\alpha + \sum_m \int_0^\infty kdk\mathrm{e}^{-\mathrm{i}m\phi}J_m(k\rho)A_m^\alpha(k)\cosh(kz) \tag{1.27}$$

$$\Phi_\alpha^{out} = \Phi_\alpha + \sum_m \int_0^\infty kdk\mathrm{e}^{-\mathrm{i}m\phi}J_m(k\rho)B_m^\alpha(k)Exp(-k|z|) \tag{1.28}$$

where $J_m(k\rho)$ is the Bessel function of order m, and Φ_α is the α-exciton electric potential. After applying the boundary conditions at the surface of the QW, the coefficients A_m^α and B_m^α are

$$A_m^\alpha(k) = \left(\frac{\exp\left(-|k\,|\,L_{QW}\right)}{\cosh\left(|k\,|\,L_{QW}\right)}\right)B_m^\alpha(k) \tag{1.29}$$

$$B_m^\alpha(k) = \frac{(\varepsilon_0 - \varepsilon_{QW})h_m^\alpha(|k|)}{k(\varepsilon_{QW}\tanh\left(|k\,|\,L_{QW}\right) + \varepsilon_0)e^{-|k\,|\,L_{QW}}} \tag{1.30}$$

where $h_m^\alpha(|k|)$ is defined as

$$h_m^\alpha(|k|) = \frac{1}{(2\pi)}\int_0^{2\pi}\int_0^{\infty} d\varphi\rho d\rho \mathrm{e}^{\mathrm{i}m\varphi}J_m(k\rho)\left[\frac{\partial\Phi_\alpha}{\partial z}\right]_{z=L_{QW}} \tag{1.31}$$

For an exciton in the z-direction, the non-zero coefficient is

$$B_0^z(k) = \left(\frac{ed_{exc}}{\varepsilon_{QW}}\right)\frac{(\varepsilon_{QW} - \varepsilon_0)}{(\varepsilon_{QW}\tanh\left(kL_{QW}\right) + \varepsilon_0)} \tag{1.32}$$

and the electric potential is

$$\Phi_z^{out} = \left(\frac{ed_{exc}}{\varepsilon_{QW}}\right)\frac{z}{(\rho^2 + z^2)^{\frac{3}{2}}} + \int_0^\infty kdkJ_0(k\rho)B_0^z(k)Exp(-k|z|) \tag{1.33}$$

Thus, in the long distance approximation, the coefficient B and the electric potential are simplified as

$$B_0^z(k) \approx \left(\frac{ed_{exc}}{\varepsilon_{QW}}\right)\frac{(\varepsilon_{QW} - \varepsilon_0)}{\varepsilon_0} \tag{1.34}$$

$$\Phi_z^{out} = \left(\frac{ed_{exc}}{\varepsilon_{eff}}\right)\frac{z}{(\rho^2 + z^2)^{\frac{3}{2}}} \tag{1.35}$$

where ε_{eff} is the effective dielectric constant defined as

$$\varepsilon_{eff} = \varepsilon_0 \tag{1.36}$$

In the case of an exciton in the x-direction, the non-zero B coefficients are $B_1^x(k)$ and $B_{-1}^x(k)$, where $B_1^x(k) = B_{-1}^x(k)$ and

$$B_1^x(k) = \frac{1}{2}\left(\frac{ed_{exc}}{\varepsilon_{QW}}\right)\frac{(\varepsilon_{QW} - \varepsilon_0)}{(\varepsilon_{QW}\tanh\left(kL_{QW}\right) + \varepsilon_0)} \tag{1.37}$$

the outside electric potential is

$$\Phi_x^{out} = \left(\frac{ed_{exc}}{\varepsilon_{QW}}\right)\frac{\rho\cos(\phi)}{(\rho^2+z^2)^{\frac{3}{2}}} + 2\cos(\phi)\int_0^\infty kdkJ_1(k\rho)B_1^x(k)Exp(-k|z|) \quad (1.38)$$

In the long distance approximation, the coefficient B and the electric potential are simplified into

$$B_0^x(k) \approx \frac{1}{2}\left(\frac{ed_{exc}}{\varepsilon_{QW}}\right)\frac{(\varepsilon_{QW}-\varepsilon_0)}{\varepsilon_0} \quad (1.39)$$

$$\Phi_x^{out} = \left(\frac{ed_{exc}}{\varepsilon_{eff}}\right)\frac{\rho\cos(\phi)}{(\rho^2+z^2)^{\frac{3}{2}}} \quad (1.40)$$

where ε_{eff} is the effective dielectric constant defined as

$$\varepsilon_{eff} = \varepsilon_0 \quad (1.41)$$

Similarly, for an exciton in the y-direction, the non-zero B coefficients are $B_{-1}^y(k)$ and $B_1^y(k)$, where $B_{-1}^y(k) = -B_1^y(k)$ and

$$B_1^y(k) = \frac{i}{2}\left(\frac{ed_{exc}}{\varepsilon_{QW}}\right)\frac{(\varepsilon_{QW}-\varepsilon_0)}{(\varepsilon_{QW}\tanh(kL_{QW})+\varepsilon_0)} \quad (1.42)$$

with the electric potential given by

$$\Phi_y^{out} = \left(\frac{ed_{exc}}{\varepsilon_{QW}}\right)\frac{\rho\sin(\phi)}{(\rho^2+z^2)^{\frac{3}{2}}} - i2\sin(\phi)\int_0^\infty kdkJ_1(k\rho)B_1^y(k)Exp(-k|z|) \quad (1.43)$$

Thus, in the long distance approximation, the coefficient B and the outside electric potential are

$$B_1^y(k) \approx \frac{i}{2}\left(\frac{ed_{exc}}{\varepsilon_{QW}}\right)\frac{(\varepsilon_{QW}-\varepsilon_0)}{\varepsilon_0} \quad (1.44)$$

$$\Phi_y^{out} = \left(\frac{ed_{exc}}{\varepsilon_{eff}}\right)\frac{\rho\sin(\phi)}{(\rho^2+z^2)^{\frac{3}{2}}} \quad (1.45)$$

where ε_{eff} is the effective dielectric constant defined as

$$\varepsilon_{eff} = \varepsilon_0 \quad (1.46)$$

Table 1.1 Effective dielectric constant expressions for NP, NW, and QW cases in the long distance approximation

α-direction	NP	NW	QW
x	$\varepsilon_{eff} = \frac{\varepsilon_{NP} + 2\varepsilon_0}{3}$	$\varepsilon_{eff} = \frac{\varepsilon_{NW} + \varepsilon_0}{2}$	$\varepsilon_{eff} = \varepsilon_0$
y	$\varepsilon_{eff} = \frac{\varepsilon_{NP} + 2\varepsilon_0}{3}$	$\varepsilon_{eff} = \varepsilon_0$	$\varepsilon_{eff} = \varepsilon_0$
z	$\varepsilon_{eff} = \frac{\varepsilon_{NP} + 2\varepsilon_0}{3}$	$\varepsilon_{eff} = \frac{\varepsilon_{NW} + \varepsilon_0}{2}$	$\varepsilon_{eff} = \varepsilon_0$

This table follows the geometries given in Fig. 1.1 [Reprinted (adapted) with permission from Ref. [1] (Copyright 2013 American Chemical Society)]

A summary for the effective dielectric constant, for the long distance approximation, is given in Table 1.1. Table 1.1 shows the screening factor in the electric potential for different confinement geometries, which corresponds to the NP, NW, and QW cases. This screening factor comes from the boundaries conditions of the electric potential at the interface between the nanostructure (NP, NW, and QW) and the medium. For example, the screening factor for the NP case is the same for an exciton in the x-, y- and z-direction because of its spherical symmetry. In the cylindrical symmetry (NW case), an exciton in the cylindrical main axis does not have any screening factor. However, an exciton perpendicular to the cylindrical main axis has a screening factor as shown in Table 1.1. In the QW case, the screening factor is the same for the x-, y- and z-direction because the QW was considered infinitesimal thin. Table 1.1 follows the geometries sketched in Fig. 1.1a.

Figure 1.1 depicts the total and long distance approximation electric potentials for a z-exciton along the z axis. Figure 1.1b shows electric potentials in both the total and long distance approximation for a z-exciton inside an NP. It can be observed that both electric potentials overlap with each other because of the spherical symmetry of the NP nanostructure. The total and long distance approximation electric potentials for a z-exciton in a NW are depicted in Fig. 1.1c. In close proximity to the NW surface, the long distance approximation underestimates the exciton electric potential, as it is shown in Fig. 1.1c. In the QW case, the long distance approximation overestimates the exciton electric potential in the close proximity to the QW surface (Fig. 1.1d). This is an opposite effect compared to the NW case. These underestimation and overestimation of the electric potential, for NW and QW, respectively, is due to the fact that at short distances the long distance approximation do not apply and higher effects need to be considered. However, in all cases, at long distances the total electric potential converges into the long distance approximation (Fig. 1.1b–d).

Reference

1. P.L. Hernández-Martínez, A.O. Govorov, H.V. Demir, Generalized theory of Förster-type nonradiative energy transfer in nanostructures with mixed dimensionality. J. Phys. Chem. C **117**, 10203–10212 (2013)